

Quantum Chemistry at Finite Temperature

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Abstract

In this article, we present emerging fields of quantum chemistry at finite temperature. We discuss its recent developments on both experimental and theoretical fronts. First, we describe several experimental investigations related to the temperature effects on the structures, electronic spectra, or bond rupture forces for molecules. These include the analysis of the temperature impact on the pathway shifts for the protein unfolding by atomic force microscopy (*AFM*), the temperature dependence of the absorption spectra of electrons in solvents, and the temperature influence over the intermolecular forces measured by the *AFM*. On the theoretical side, we review advancements made by the author in the coming fields of quantum chemistry at finite temperature. Starting from the *Bloch* equation, we have derived the sets of hierarchy equations for the reduced density operators in both canonical and grand canonical ensembles. They provide a law according to which the reduced density operators vary in temperature for the identical and interacting many-body systems. By taking the independent particle approximation, we have solved the equations in the case of a grand canonical ensemble, and obtained an energy eigenequation for the molecular orbitals at finite temperature. The explicit expression for the temperature-dependent *Fock* operator is also given. They

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form a mathematical foundation for the examination of the molecular electronic structures and their interplay with finite temperature. Moreover, we clarify the physics concerning the temperature effects on the electronic structures or processes of the molecules, which is crucial for both theoretical understanding and computation. Finally, we summarize our discussion and point out some of the theoretical and computational issues in the fields of quantum chemistry at finite temperature for the future exploration.

Keywords Quantum chemistry at finite temperature; temperature dependent; polymers; protein folding; protein unfolding; intermolecular forces; solvated electrons; molecular crystals

1 Introduction

The history for quantum chemistry development is almost synchronous to that of quantum mechanics itself. It begins with *Heitler* and *London*'s investigation of the electronic structure for H_2 molecule shortly after the establishment of the wave mechanics for quantum particles [1]. There are two major types of molecular electronic theories: valence bond approach *vs.* molecular orbital method with the latter being the popular one for the present study. It has gone through the stages from the evaluation of molecular integrals via a semiempirical way to the one by an *ab initio* method. The correlation issue is always a bottleneck for the computational quantum chemistry and is under intensive examination for over fifty years [2]. For large molecular systems such as biomolecules and molecular materials, the development of the combined *QM/MM* approach, the pseudopotential method and the linear scaling algorithm has significantly advanced our understanding of their

structure and dynamics. There are about eight *Nobel* prize laureates whose researches are related to the molecular electronic structure theory. This not only recognizes the most eminent scientists who have made the outstanding contributions to the fields of quantum chemistry, but more importantly, it indicates the essential roles the electronic structure theory has been playing in the theoretical chemistry as well as for the whole areas of molecular sciences [2]. Nowadays, quantum chemistry has been becoming a maturing science [3, 4].

Nevertheless, the modern fields of quantum chemistry are only part of the stories for the molecular electronic structure theory. From the pedagogical points of view, the quantum mechanics based on which the traditional quantum chemistry is built is a special case of more general quantum statistical mechanics [5, 6, 7]. In reality, the experimental observations are made under the conditions with thermodynamic constraints. Henceforth, there is a need to extend the contemporary areas of quantum chemistry to the realm of, for instance, finite temperature [5, 6, 7].

Indeed, many experimental investigations in various fields and for different systems have already shown the temperature or pressure effects on their microscopic structures [8-31, 50-58, 64, 72-88]. The polymeric molecule is one of the most interesting systems for this sort of studies [8-17]. The experimental measurement on the absorption spectra, photoluminescence (*PL*), and photoluminescence excitation (*PLE*), and spectral line narrowing (*SLN*) for the *PPV* and its derivatives all show the same trend of the blue shift with an increasing temperature [8, 9, 10]. This attributes to the temperature dependence of their very rich intrinsic structures such as the

vibronic coupling [15, 16, 17]. The experimental inquiry of the temperature impacts on the biomolecules started in the late nineteenth century [18, 19]. Most recently, it has been extended to the study of folding and unfolding of proteins or *DNAs* [20, 21, 22]. In addition to the observed patterns for the unfolding forces with respect to the extension or temperature, it has been proved that the temperature-induced unfolding is another way for the examination of mechanisms or pathways of protein folding or unfolding processes [20-24]. The newest related development is on the *AFM* measurement made by *Lo et al.* of the intermolecular forces for the biotin-avidin system in the temperature range from 286 to 310K [64]. It has shown that an increase of temperature will almost linearly decrease the strength of the bond rupture force for the individual biotin-avidin pair. The analysis of the temperature influences over the absorption spectra of the solvated electron began in the 1950's and it is still of current interest. A striking effect is that an increasing temperature will cause the positions of their maximal absorption red shift [72-86].

In two papers recently published, we have deduced an energy eigenequation for the molecular orbitals [5, 6]. It is the extension from the usual *Hartree – Fock* equation at zero temperature to the one at any finite temperature [89, 90]. It opens an avenue for the study of the temperature impacts on the electronic structures as well as their interplay with the thermodynamic properties. In the third section, we will present this equation and give the details for its derivation. We will also expound the physics concerning the effects from temperature and classify them into two types. The one is at the single orbital level and the other is really an *N*-body effect. In the

next section, we will show four major types of experiments related to the investigation of the temperature influences over the microscopic structures of molecular systems. In the final section, we will discuss and analyze our presentations, and point out both theoretical and computational issues for the future examination.

2 Experimental Development

In this section, we focus our description of the experimental investigations related to the temperature effects on the bondings, structures, or electronic spectra of molecules. We choose four kinds of the most recent developments in these fields which are of chemical, biological, or material interests.

2.1 Temperature effects on geometric structure and UV-visible electronic spectra of polymers

The first important systems where the major issues related to the temperature influences over the geometric structures and electronic spectra are the polymeric molecules. Many experimental inquiries and some theoretical works already exist in the literature [8-17]. However, how temperature changes the microscopic structures of the polymers are still not completely understood and there are many unresolved problems in interpreting their electronic spectra. We list here a few very interesting experimental examinations for the purpose of demonstration.

The poly(*p*-phenylenevinylene)(*PPV*) is one of the prototype polymeric systems for the study of their various mechanical, electronic, and optical

properties. The impact from temperature on the absorption spectra, the photoluminescence (*PL*), and the photoluminescence excitation (*PLe*) of the *PPV* has also been investigated both experimentally and theoretically [8, 9, 10]. In an experiment performed by *Yu et al.*, the absorption spectra are measured for the *PPV* sample from the temperature 10 to 330K. The details of the experiment are given in their paper [10]. The resulting spectra for the absorption at $T = 80$ and 300K are shown in Figure 1 of that paper. We see that there is a pronounced change in the spectra when increasing the temperature. They also study the *PL* and *PLe* spectra for the *PPV*. The measured *PL* spectra at two temperatures: 77 and 300K are demonstrated in Figure 3, and the *PLe* spectra at those temperatures are depicted in Figure 4 of the paper [10]. They both show the dramatic changes of the band blue shift when the temperature is increased. Similar studies have also been carried out before by the other groups [8, 9]. They observed the similar behaviors.

Another interesting analysis is related to the temperature effects on the spectral line narrowing (*SLN*) of the poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene)(*MEH - PPV*) spin-coated from either *THF* or *CB* solvents [12]. In the experiment conducted by *Sheridan et al.*, the *SLN* is measured together with the absorption and *PL* as shown in Fig. 1 of their paper. It is found that the same trend of the *SLN* blue shift is observed as that for the absorption and *PL* with an increasing temperature. They attribute this to the same reason of the electronic structure modification resulting from the variation of temperature.

2.2 Temperature effects on structure, dynamics, and folding/unfolding of biomolecules

Biomolecules are complex systems, featuring a large molecular size, a heterogeneity of atomic constituents and a variety of conformations or configurations. Their energy landscapes thereby exhibit multiple substates and multiple energy barriers, and vary in size for the barrier heights [25, 26, 27, 28, 29]. The temperature should have a strong influence over their structure and dynamics including the folding or unfolding [18-58]. This effect could be either from the fluctuation of thermal motions of the molecules or due to the redistribution of the electronic charge as we will discuss in the next section.

The experimental observation of the temperature impact on the microscopic structure of biological systems dates back to the very early days. One focus, for example, is on the measurement of the elastic properties of the human red blood cell membrane as a function of temperature [18, 19]. Another related investigation is about the influence over the thermal structural transition of the young or unfractionated red blood cells due to the involvement of the protein spectrin which might modify the spectrin-membrane interaction [30, 31]. Most recently, the atomic force microscopy (*AFM*) has been used to detect the impact from the variation of temperature on the spectrin protein unfolding force as well as on the bond rupture force for the biotin-avidin system [20, 21, 22, 64].

The *AFM* is a surface imaging technique with an atomic-scale resolution capable of measuring *any* types of the forces as small as 10^{-18} N. It combines the principles of the scanning tunnelling microscopes (*STM*) and the stylus profilometer, and therefore can probe the surfaces of both con-

ducting and nonconducting samples [32, 33]. The imaging on soft materials such as biomolecules with the *AFM* has been accomplished beginning in the 1980's [34, 35, 36]. Recently, it has been applied to measure the adhesive forces and energies between the biotin and avidin pair as we will show in the next subsection [37, 38, 39, 40]. Unlike other experimental techniques, the *AFM* features a high precision and sensitivity to probe the surface with a molecular resolution, and can be done in physiological environments.

In an *AFM* investigation of the mechanical unfolding of titin protein, for example, the restoring forces all show a sawtooth like pattern with a definite periodicity. It reveals much information about the mechanism of the unfolding processes [43, 44]. The observed pattern, in addition to a fit of a worm-like chain model, has also been verified by the steered molecular dynamics or Monte carlo simulations [45, 46]. Similar study has been extended to other systems [47, 48, 49].

The same kind of experiments has also been performed by varying temperature. In the experiment carried out by Spider and Discher et al. [22], the spectrin protein is chosen for the *AFM* study at different temperatures. Thousands of tip-to-surface contacts are conducted for a given temperature because of the statistical nature of the *AFM* measurement. The observed curve for the relation between the unfolding force and extension shows the similar sawtooth pattern for all temperatures. In addition, the tandem repeat unfolding events are more favored at lower temperature as demonstrated in the unfolding length histograms. Most striking is that the unfolding forces show a dramatically nonlinear decreasing relation as the temperature T approaches the transition temperature T_m . This is shown in Figure 3B of the

paper [22].

Similar behaviors regarding the force-temperature dependence have also been observed via either *AFM* or optical tweezers for the forced overstretching transition for the individual double-stranded *DNA* molecules [20, 21, 50, 51].

Some other interesting experiments which illustrate the effects from temperature on the microscopic structures of biomolecules have also been performed even though the detailed physical origins of the impacts (from either the electrons or the molecules) have not been specified [53, 54, 55, 56, 57, 58]. In a circular dichroism (*CD*) spectra and high resolution *NMR* study, for instance, it shows that the secondary structure of the Alzheimer β (12-28) peptide is temperature-dependent with an extended left-handed 3_1 helix interconverting with a flexible random coil conformation [53]. Another example is related to the analysis of the temperature-dependent interaction of the protein *Ssh10b* with a *DNA* which influences the *DNA* topology [54, 55, 56]. The analysis from the heteronuclear *NMR* and site-directed mutagenesis indicates that the *Ssh10b* exists as a dimer: *T* form and *C* form. Their ratio is determined by the *Leu*⁶¹ – *Pro*⁶² peptide bond of the *Ssh10b* which is sensitive to temperature.

2.3 Temperature effects on intermolecular forces

The analysis of the general issues related to the temperature effects on the microscopic structures has been most recently extended to the realm of intermolecular forces. Since the usual intermolecular forces such as hydrogen bonds, *van der Waals* forces, ionic bonds, and hydrophobic interactions are

weak and typically of the order of 0.1 eV or 4.0 kT at the physiological temperature, the variation of temperature will thereby have a very strong influence over the strength of these forces.

The first experimental investigation on the temperature-dependent inter-molecular forces is for the biotin-avidin system and by an *AFM* measurement [64]. The biotin-avidin complex is a prototypical receptor and ligand system with the biotin binding strongly up to four avidin proteins [59, 60, 61, 62, 63]. They have an extremely high binding affinity, and therefore serves as a model system for various experimental examinations. In the experiment carried out in *Beebe's* group [64], the receptor avidin is attached to the *AFM* tip and linked to the agarose bead functionalized with the biotin. The temperature of the entire *AFM* apparatus is varied at a range from 286 to 310K. In addition, the loading rate is kept very slow so that the thermal equilibrium for the biotin-avidin pairs is assumed. The forces expected to be determined is the rupture force F_i between the individual biotin-avidin pair which is defined as the maximum restoring force [64]. In an actual *AFM* experiment, however, the total adhesive force between the tip and substrate is measured. It is a sum of the finite number n of the interactions between each biotin and avidin pair. To extract the individual and average bond rupture, a statistical method has been developed in *Beebe's* group [40, 41, 65, 66, 67]. They assume a *Poisson* distribution for the number n of the discrete rupture forces or linkages from multiple measurements, and have obtained the single force F_i at different temperatures. The result is shown in Figure 3 of the paper [64]. We see that the individual rupture force F_i for the biotin-avidin pair is decreased by about five-fold in strength when the temperature is increased

from 286 to 310K.

To interpret the observed temperature impact on the biotin-avidin forces, *Peebe*'s group has performed a thermodynamic analysis [64]. Based on the simple models and arguments [68, 69], they have come out an equation that connects the square of the single bond-rupture force F_i to the absolute temperature T as follows,

$$F_i^2 = 2\Delta E^\ddagger k_{bond} - 2k_B T k_{bond} \ln \left(\frac{\tau_R}{\tau_D} \right) \quad (1)$$

where the k_{bond} is the force constant of the individual biotin-avidin pair, and the time τ_R is the characteristic time needed to break n pairs of those forces. The E^\ddagger is the energy required to remove the biotin from avidin's strongest binding site and the corresponding time is τ_D . More details on this analysis can be found in the paper [64]. The relation between the square of the force F_i and the temperature T is also plotted as Figure 5 in that paper. Therefore, from the relation (1) and this figure, the information about the stiffness of the ligand and receptor bond and the critical binding energy, etc. can be obtained. Obviously, what we need at present is a microscopic theory which can account for all these relations and properties.

2.4 Temperature effects on absorption spectra of electrons in solvents

The structure and dynamics of the solute in solvents is one of the most important fields in chemistry since most of the chemical reactions occur in solution phases. In the meantime, it is also one of the most challenging areas in theoretical chemistry with many unsettled issues. The variation of temperature in the measurement of absorption spectra of solvated electron

in various solvents has proved to be a useful means for the understanding of the solvation processes [71-85].

There are several experimental techniques available for this type of inquiry with the pulse radiolysis being the one most commonly used. There are also several research groups conducting the similar experimental investigations and obtaining the consistent results relating to the temperature effects on the optical absorption spectra of the solvated electron in solvents. In a recent experiment carried out in *Katsumura's* group, for example, the pulse radiolysis technique is employed to study the optical absorption spectra of the solvated electron in the ethylene glycol at different temperatures from 290 to 598K at a fixed pressure of 100 atm. In addition to the faster decay of absorptions, it is found that, their maximal positions shift to the red with the increasing temperature as shown in Figures 1 to 3 of the paper [82]. This is in contrast to the situation for the electronic spectra of the polymers. They also point out the need to quantify the change of the density in the experiment in order to really understand the observed results.

The same type of experiments has been extended to the examination of the optical absorption spectra for Ag^0 and Ag_2^+ in water by varying temperature, and similar results have been obtained [81].

3 Theoretical Development

Having presented four different types of experiments above, we can observe that the investigation of the temperature effects on the microscopic structures of molecules is a very interesting and sophisticated field. More need to be

probed and understood. Even though the experimental analysis has been for a long time, very limited number of the related theoretical works is available, especially at the first-principle level. In other words, the quantum chemistry at finite temperature is not a well-established field [5, 6, 7].

It is true that the influence of temperature on the microscopic structures is a complicated phenomenon. There exists different functioning mechanisms. One consideration is that the variation of temperature, according to the Fermi-Dirac statistics, will change the thermal probability distribution of single-particle states for a free electron gas. It is expected that similar situation should occur for an interacting electron system, and therefore its microscopic structure will be correspondingly altered. Another consideration is that, for molecules or solids, the thermal excitation will cause the change of the time scales for the molecular motions. This will most likely bring about the transitions of the electronic states, and therefore lead to the breakdown of the Born-Oppenheimer approximation. The electron-phonon interaction is a fundamental topic in solid state physics and its temperature dependence is well-known. As a result, the variation of temperature will change the strength of the coupling between the electronic and molecular motions. Nevertheless, we tackle the issues pertaining to the temperature effects in a simpler way. We treat only an identical and interacting *fermion* system. Or we neglect the coupling of the electronic motion with those of the nucleus in the molecules or solids. We expect that some sort of the general conclusions will come out from this analysis. As a matter of fact, this is the approach commonly admitted in a non-adiabatic molecular dynamics study, in which purely solving the eigenequation for the electrons will provide the

reference states for the examination of the coupling between the electronic and nuclear motions of the molecules.

In the following, we will present self-consistent eigenequations within the framework of the density operators in equilibrium statistical mechanics which decides the molecular orbitals at a given temperature.

3.1 Hierarchy Bloch equations for reduced density operators in canonical ensemble

We consider an identical and interacting N -particle system. In a canonical ensemble, its N th-order density operator takes the form

$$D^N = \exp(-\beta H_N), \quad (2)$$

and satisfies the *Bloch* equation [91, 92]

$$-\frac{\partial}{\partial \beta} D^N = H_N D^N, \quad (3)$$

where

$$H_N = \sum_{i=1}^N h(i) + \sum_{i<j}^N g(i, j), \quad (4)$$

is the *Hamiltonian* for the N particle system composed of one-particle operator h and two-body operator g . The β is the inverse of the product of *Boltzmann* constant k_B and absolute temperature T .

Since the *Hamiltonian* (4) can be written as a reduced *two*-body operator form, the second-order reduced density operator suffices to describe its N (≥ 2) particle quantum states. A p th-order reduced density operator is generally defined by [93, 94]

$$D^p = L_N^p(D^N), \quad (5)$$

where L_N^p is the contraction operator acting on an N th-order tensor in the N -particle *Hilbert* space V^N . The trace of the D^p gives the partition function,

$$\text{Tr}(D^p) = Z(\beta, V, N). \quad (6)$$

Rewrite the *Hamiltonian* in a form

$$H_N = H_1^p + \sum_{j=p+1}^N h(i) + \sum_{i=1}^p \sum_{j=p+1}^N g(i, j) + \sum_{i < j (i \geq p+1)}^N g(i, j), \quad (7)$$

where

$$H_1^p = \sum_{i=1}^p h(i) + \sum_{i < j}^p g(i, j), \quad (8)$$

and apply the contraction operator L_N^p on both sides of the Eq. (3), we develop an equation that the p th-order density operator satisfies [5]

$$\begin{aligned} -\frac{\partial}{\partial \beta} D^p &= H_1^p D^p + (N-p) L_{p+1}^p [h(p+1) D^{p+1}] + (N-p) L_{p+1}^p \left[\sum_{i=1}^p g(i, p+1) D^{p+1} \right] + \\ &+ \binom{N-p}{2} L_{p+2}^p [g(p+1, p+2) D^{p+2}]. \end{aligned} \quad (9)$$

It provides a law according to which the reduced density operators vary in terms of the change of temperature.

3.2 Hierarchy Bloch equations for reduced density operators in grand canonical ensemble

The above scheme for deducing the equations for the reduced operators can be readily extended to the case of a grand canonical ensemble. It is a more general one with a fluctuating particle number N . In this ensemble, the density operator is defined in the entire *Fock* space

$$F = \sum_{N=0}^{\infty} \oplus V^N,$$

and is written as the direct sum of the density operators $D_G(N)$ associated with the N -particle *Hilbert* space V^N ,

$$D_G = \sum_{N=0}^{\infty} \oplus D_G(N), \quad (10)$$

where

$$\begin{aligned} D_G(N) &= \exp[-\beta(H - \mu N)], \\ &= \exp(-\beta \bar{H}), \end{aligned} \quad (11)$$

and

$$\bar{H} = H - \mu N, \quad (12)$$

is called the grand *Hamiltonian* on V^N . The form of the *Hamiltonian* H has been given by Eq. (4) and the μ is the chemical potential. The corresponding p th-order reduced density operator is therefore defined as

$$D_G^p = \sum_{N=p}^{\infty} \oplus \binom{N}{p} L_N^p[D_G(N)] \quad (13)$$

with the trace given by

$$Tr(D_G^p) = \left\langle \binom{N}{p} \right\rangle D_G^0, \quad (14)$$

and

$$D_G^0 = \Xi(\beta, \mu, V). \quad (15)$$

The $\Xi(\beta, \mu, V)$ is the grand partition function.

In a similar manner, we can also derive the hierarchy equations that the reduced density operators in the grand canonical ensemble obey [6]

$$\begin{aligned} -\frac{\partial}{\partial \beta} D^p &= \bar{H}_1^p D^p + (p+1) L_{p+1}^p [\bar{h}(p+1) D^{p+1}] + (p+1) L_{p+1}^p \left[\sum_{i=1}^p g(i, p+1) D^{p+1} \right] + \\ &+ \binom{p+2}{2} L_{p+2}^p [g(p+1, p+2) D^{p+2}], \end{aligned} \quad (16)$$

where

$$\bar{H}_1^p = \sum_{i=1}^p \bar{h}(i) + \sum_{i<j}^p g(i, j), \quad (17)$$

and

$$\bar{h}(i) = h(i) - \mu. \quad (18)$$

It gives us a law with which the reduced density operators in the grand canonical ensemble vary in temperature.

3.3 Orbital approximation and Hartree-Fock equation at finite temperature

The Eqs. (9) and (16) define a set of *hierarchy* equations that establish the relation among the reduced density operators D^p , D^{p+1} , and D^{p+2} . They can be solved either in an exact scheme or by an approximate method. The previous investigation of N electrons with an independent particle approximation to the *Schrödinger* equation for their *pure* states has lead to the *Hartree – Fock* equation for the molecular orbitals [95-101]. We thereby expect that the same approximate scheme to the reduced *Bloch* equations (9) or (16), which hold for more general mixed states, will yield more generic eigenequations than the usual *Hartree – Fock* equation for the molecular orbitals.

We consider the case of a grand canonical ensemble. For $p = 1$, Eq. (16) reads

$$-\frac{\partial}{\partial \beta} D^1 = \bar{H}_1 D^1 + \frac{Tr(\bar{h} D^1)}{D^0} D^1 - \frac{1}{D^0} D^1 \bar{h} D^1 + 2L_2^1 [g(1, 2) D^2] + 3L_3^1 [g(2, 3) D^3]. \quad (19)$$

Under the orbital approximation, above second-order and third-order reduced

density operators for the electrons can be written as

$$D^3 = D^1 \wedge D^1 \wedge D^1 / (D^0)^2 \quad (20)$$

and

$$D^2 = D^1 \wedge D^1 / D^0. \quad (21)$$

These are the special situations for the statement that a p th-order reduced density matrix can be expressed as a p -fold *Grassmann* product of its first-order reduced density matrices. With this approximation, the last two terms of Eq. (19) can be evaluated in a straightforward way as follows

$$2L_2^1 [g(1, 2)D^2] = (J - K)D^1, \quad (22)$$

and

$$3L_3^1 [g(2, 3)D^3] = \frac{Tr(gD^2)}{D^0} - \frac{1}{D^0} D^1 (J - K) D^1, \quad (23)$$

where

$$J = Tr_2 [g \cdot D^1(2; 2)] / D^0, \quad (24)$$

and

$$K = Tr_2 [g \cdot (2, 3) \cdot D^1(2; 2)] / D^0, \quad (25)$$

are called the *Coulomb* and exchange operators, respectively. With (2, 3) being the exchange between the particle 2 and 3, the action of the K on the reduced density operator is

$$\begin{aligned} K \cdot D^1(3; 3) &= Tr_2 [g \cdot (2, 3) \cdot D^1(2; 2)] / D^0 \cdot D^1(3; 3) \\ &= Tr_2 [g \cdot D^1(3; 2) \cdot D^1(2; 3)] / D^0. \end{aligned} \quad (26)$$

Substitution of Eqs. (22) and (23) into Eq. (19) results in the *Bloch* equation for the first-order reduced density matrix of the N interacting electrons under

the orbital approximation,

$$-\frac{\partial}{\partial\beta}D^1 = (F - \mu)D^1 + \left(\frac{Tr \bar{h}D^1}{D^0} + \frac{Tr gD^2}{D^0} \right) D^1 - \frac{1}{D^0}D^1(F - \mu)D^1, \quad (27)$$

where

$$F = h + J - K, \quad (28)$$

is called the *Fock* operator at finite temperature. Redefine the normalized first-order reduced density operator

$$\rho^1 = D^1/D^0, \quad (29)$$

we can simplify above equation into

$$-\frac{\partial}{\partial\beta}\rho^1 = (F - \mu)\rho^1 - \rho^1(F - \mu)\rho^1. \quad (30)$$

Furthermore, from Eq. (30) and its conjugate, we get

$$F\rho^1 - \rho^1 F = 0, \quad (31)$$

which indicates that the *Fock* operator F and the first-order reduced density matrix ρ^1 commute. They are also *Hermitian*, and therefore have common eigenvectors $\{|\phi_i\rangle\}$. These vectors are determined by the following eigen equation for the *Fock* operator,

$$F|\phi_i\rangle = \epsilon_i|\phi_i\rangle. \quad (32)$$

It is the eigenequation for the molecular orbitals at finite temperature.

The first-order reduced density operator is correspondingly expressed as

$$\rho^1 = \sum_i \omega(\beta, \mu, \epsilon_i) |\phi_i\rangle \langle \phi_i|, \quad (33)$$

where $\omega(\beta, \mu, \epsilon_i)$ is the thermal probability that the orbital is found to be in the state $\{|\phi_i\rangle\}$ at finite temperature T . Substituting Eq. (33) into Eq. (30), we can obtain the equation this thermal probability $\omega(\beta, \mu, \epsilon_i)$ satisfies,

$$-\frac{\partial}{\partial\beta}\omega(\beta, \mu, \epsilon_i) = (\epsilon_i - \mu)\omega(\beta, \mu, \epsilon_i) - (\epsilon_i - \mu)\omega^2(\beta, \mu, \epsilon_i). \quad (34)$$

Its solution has the same usual form of the *Fermi – Dirac* statistics for the free electron gas as follows,

$$\omega(\beta, \mu, \epsilon_i) = \frac{1}{1 + e^{\beta(\epsilon_i - \mu)}}, \quad (35)$$

with the energy levels $\{\epsilon_i\}$ determined by Eq. (32).

4 Discussion, Summary and Outlook

In this paper, we have presented both experimental and theoretical developments related to the temperature impacts on the microscopic structures and processes for the molecules.

In the theoretical part, we have depicted the sets of hierarchy *Bloch* equations for the reduced statistical density operators in both canonical and grand canonical ensembles for the identical fermion system with a two-body interaction. We have solved the equations in the latter case under a single-orbital approximation and gained an energy eigenequation for the single-particle states. It is the extension of usual *Hartree – Fock* equation at absolute zero temperature to the one at any finite temperature. The average occupation number formula for each single-particle state is also obtained, which has the same analytical form as that for the free electron gas with the single-particle

state energy determined by the *Hartree – Fock* equation at finite temperature (32).

From Eqs. (24), (25) and (28), we see that the *Coulomb* operator J , the exchange operator K , and therefore the *Fock* operator F are both coherent and incoherent superpositions of the single-particle states. They are all temperature-dependent through an incoherent superposition factor, the *Fermi – Dirac* distribution, $\omega(\beta, \mu, \epsilon_i)$. Therefore, the mean force or the force field, and the corresponding microscopic structures are temperature-dependent.

We have expounded the physics relating to the temperature effects on the electronic structures or processes for the molecules. These effects can be either at the single-electron level or of the N -body excitation. This is very critical for our understanding and computation of the temperature influences over the molecular structures. From this analysis, for example, we can conclude that the temperature should have a stronger effect on the transition states for the molecules. Accordingly, the change of the chemical reactivity might come from the alternation of the electronic states due to the variation of temperature. We expect that this sort of the changes involving configuration mixing will be very common for the systems we are discussing here. Therefore, it will be a very significant work to develop or test the corresponding multireference theory for the molecular orbitals or electronic structures at finite temperature [2, 102, 103, 104, 105]. More general or standard theoretical explorations are expected [3].

On the experimental side, we have exposed four major fields of investigation of chemical, biomolecular, or material importance, which demonstrate

the temperature impacts on their structures, spectra, or bond rupture forces.

The complete determination of the geometric structures and electronic spectra of the polymeric molecules is a very difficult task. As has been stated in papers [16, 17], there are many different elements contributing to the change of the spectra. At present, we focus on the examination of the effect from temperature. We have showed that it can alter both the shapes and positions of the absorption and other spectra for the *PPV* and its derivatives. As has been analyzed, the increase of temperature will bring about the excitation of the vibrational, rotational and liberal motions, which might also lead to the electronic transition. The *Huang – Rhys* parameter has been introduced to describe the strength of the coupling between the electronic ground- and excited-state geometries. Furthermore, it has been observed that this factor is an increasing function of temperature [8, 9, 10]. Obviously, a more detailed analysis of the electronic structure, excitation and spectroscopic signature at the first-principle level, which includes the temperature-dependent force field, is anticipated.

Temperature has proved to be a big player in both experimental and theoretical study of the structure and dynamics of biomolecules including their folding or unfolding. At a first glance, the energy gap between the *HOMO* and *LUMO* for the biomolecules should be small or comparable to the *Boltzmann* thermal energy $k_B T$ because of their very large molecular size. Therefore a change of temperature should have a strong influence over their electronic states, and consequently, the energy landscape and the related dynamics including the folding and unfolding. The experimental investigation with the *AFM* and other techniques of the temperature effect on the shift of

their unfolding pathways might have verified this type of thermal deformation of the potential energy landscape [20, 21, 22]. This is in contrast to the tilt and deformation of the energy landscape including its transition states for the biomolecules resulting from the applied mechanical forces [70].

Unfolding proteins by temperature is not just one of the classical experimental techniques for the analysis of the structure, dynamics and energetics of the biomolecules. It has also been utilized, for example, in the molecular dynamic simulation to study the structure of the transition states of *CI2* in water at two different temperatures: 298 *K* and 498 *K* [23]. The later high temperature is required in order to destabilize the native state for monitoring the unfolding as done in the real experiments. In another recent molecular dynamics simulation [24], *Karplus's* group has compared the temperature-induced unfolding with the force-stretching unfolding for two β -sandwich proteins and two α -helical proteins. They have found that there are significant differences in the unfolding pathways from two approaches. Nevertheless, in order to get more reliable results, the temperature-dependent force fields need to be developed and included in the molecular dynamics simulations. This is also the case in the theoretical investigation of protein folding since an accurate simulation of protein folding pathways requires better stochastic or temperature-dependent potentials which have become the bottleneck in structure prediction [25, 26, 27, 28, 29]. From structural points of view, the variation of temperature leads to the change of the mean force or the energy landscape, and therefore provides a vast variety of possibilities, for instance, in the protein design and engineering.

The intermolecular forces are ubiquitous in nature. They are extremely

important for the biological systems and for the existence of life. The intermolecular forces have the specificity which is responsible for the molecular recognition between the receptor and ligand, the antibody and antigen, and complementary strands of *DNA*, and therefore for the regulation of complex organization of life [106]. For these reasons, the experiment carried out in *Beebe's* group has an immediate significance. It has demonstrated that temperature can be an important factor for changing the specificity of the intermolecular forces and therefore the function of life [64]. Nevertheless, how the charge redistribution occurs due to the variation of temperature has not been interpreted, and a microscopic theory for quantifying the temperature influence over the intermolecular forces is still lacking. Since the delicate study of the intermolecular forces provides the insight into complex mechanisms of ligand-receptor binding and unbinding processes or pathways, a paramount future research is to establish the links between the intermolecular forces and the temperature within quantum many-body theory.

The theoretical exploration of the temperature effects on the optical absorption spectra of solvated electrons is still in very early stage and few published works are available [83, 84, 85, 86]. One of the earliest inquires by *Jortner* used a cavity model to simulate the solvated electron where the electron is confined to the cavity surrounded by the dielectric continuum solvent [83]. However, his investigation is not of fully microscopic in nature since he assumed a temperature dependence of phenomenological dielectric constants which were obtained from the available experimental data. In addition, the model used is too simplified and, for instance, it neglects the intrinsic structure of solvent molecules. There are a few recent examinations

on the temperature influences over the absorption spectra of the solvated electrons. They all cannot catch the full features of the experimental observations. One reason is that the physical nature for the process is not totally understood which might leads to incorrect models employed for the simulation. The other is to utilize the crude models which might have omitted some important physical effects. For example, in an analysis by *Brodsky* and *Tsarevsky* [84], they have concluded a temperature-dependence relation for the spectra which is, however, in contradiction with the experimental findings at high temperature. The quantum path-integral molecular dynamics simulation cannot produce those temperature-dependence relations observed in the experiments [85]. In a recent quantum-classical molecular-dynamics study by *Nicolas et al*, even though the temperature-dependent features of optical absorption spectra for the solvated electron in water have been recovered [86], however, they claim that the red shifts of absorption spectra with the increasing temperature observed in both experiments and calculations are due to the density effect instead of temperature. This might cast the doubt of usefulness of our present theoretical work in this area. However, after examining their work, we observe that they actually have *not* included any temperature effects on the electron in their theoretical model. These effects might be either from the *Fermi – Dirac* distribution for individual electrons or due to the electronic excitation caused by the thermal excitation of the solvent, as we have discussed previously and in paper [6]. Obviously, much finer theoretical works or more experimental investigations in this area are expected to resolve this dispute.

In addition to the systems discussed above, there are many other types

which show the temperature impacts on their microscopic structures. Either theoretical or experimental works have been done or are in progress. Examples include the study of the temperature dependence of the *Coulomb* gap and the density of states for the *Coulomb* glass, the experimental investigation of the temperature effects on the band-edge transition of *ZnCdBeSe*, and the theoretical description of the influence from temperature on the polaron band narrowing in the oligo-acene crystals [107, 108, 109].

To sum up, the quantum chemistry at finite temperature is a new and exciting field. With the combination of the techniques from modern quantum chemistry with those developed in statistical or solid state physics, it will provide us with a myriad number of opportunities for the exploration [3, 6, 104, 105, 110]¹

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